

Investigation of Chemical Transfer Processes between Atmosphere and Snow at South Pole

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Oxidation by OH is the primary atmospheric sink for many environmentally important gases, including methane (CH_4), carbon monoxide (CO), and halogenated hydrocarbons. Because of its very short lifetime, OH is not preserved in snow and ice. Hydrogen peroxide (H_2O_2) is a sink for OH, and, because it is preserved in snow and ice, concentrations of H_2O_2 preserved in ice sheets offer the potential to reconstruct past atmospheric concentrations of H_2O_2 and, hence, OH. However, to make use of the chemical archive, a quantitative understanding of the processes that control atmosphere-to-snow transfer and preservation of H_2O_2 in polar environments is required. Through a cooperative agreement with CMDL at South Pole, we have been making year-round measurements of H_2O_2 concentration in the surface and near-surface snow since November 1994. These year-round measurements in the surface snow complement more intensive, summertime measurements in the atmosphere and in snow pits and shallow cores. The summer sampling and all sample analyses at South Pole are conducted under NSF-funded grants.

Results of the nearly continuous, year-round surface-snow sampling (November 1994 through January 2001) are shown in Figure 1. Replicate samples are collected at each sampling period and error bars show the variability (1σ) of the H_2O_2 concentration between replicates. There is a distinct annual cycle in H_2O_2 concentration in the surface

snow that results from a combination of very strong changes in atmospheric concentration of H_2O_2 throughout the year [Stewart and McConnell, 1999], a strong annual temperature cycle at South Pole, and a highly nonlinear partitioning of the H_2O_2 between air and snow as a function of temperature [Conklin *et al.*, 1993; McConnell *et al.*, 1997]. Because deposition of H_2O_2 is reversible, preservation is strongly dependent on depositional parameters such as temperature and snow accumulation rate and timing [McConnell, 1997; McConnell *et al.*, 1998, Hutterli *et al.*, 2001]. By reversible we mean that some fraction of the deposited mass cycles between the snow and air until the snow is cut off from the atmosphere by burial. The net result is that while we have measured a strong decrease in H_2O_2 concentration in firn cores from South Pole representing snow deposited over the past ~30 years, much of the observed decrease is likely the result of a slow release of H_2O_2 from supersaturated layers near the surface. The decrease with depth is pronounced at South Pole because the relatively cold temperatures slow diffusion-controlled release of H_2O_2 from the snow pack and because the low snow accumulation rates allow exchange with the atmosphere for many years after the snow is deposited.

Formaldehyde (HCHO) concentrations also provide information on the atmospheric oxidation capacity, and HCHO studies in the air and snow at South Pole are integral to our overall research effort. Results of recent snow pit and shallow core studies at South Pole, in agreement with similar studies in Greenland and other Antarctic locations, show that HCHO deposition is also reversible and that exchange with the atmosphere is much greater than for H_2O_2 (M. Hutterli *et al.*, HCHO in Antarctic snow: Preservation in ice cores and air-snow exchange, submitted to *Geophysical Research Letters*, 2002). HCHO concentrations in snow samples are time-sensitive, thereby precluding year-round surface snow sampling by onsite CMDL personnel.

Year-round surface snow studies at South Pole have recently been expanded to include sampling for trifluoroacetate (TFA). TFA is the primary atmospheric degradation product of the CFC replacement HFC-134a, and there is concern about the environmental consequences of a build up of this strongly hydrophilic compound in natural waters. South Pole is a particularly appropriate location to carry out such sampling because atmospheric measurements of the primary precursor, HFC-134a, and other related compounds have been made by CMDL since ~1994 [Montzka *et al.*, 1996]. Moreover, measurements of HFC-134a in the firn air at South Pole have recently been reported [Butler *et al.*, 1999]. As with the H_2O_2 studies, the

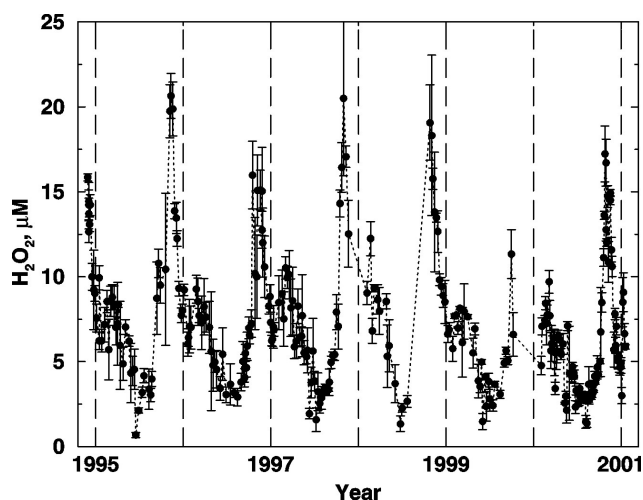


Fig. 1. Hydrogen peroxide in surface snow at South Pole. Error bars show 1 standard deviation in replicate measurements.

year-round sampling by onsite CMDL personnel complements more intensive summer snow pit sampling conducted under NSF funding. The TFA project has only started recently; therefore, no results are available at this time.

The year-round South Pole data, made possible through the cooperative agreement with CMDL, are also important for the interpretation of similar H₂O₂, HCHO, and TFA data from snow pits and shallow cores collected in summertime in West Antarctica as part of the International Trans-Antarctic Scientific Expedition (ITASE) [Frey *et al.*, 2001].

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